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FTIR study of hydration of dodecatungstosilicic acid

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The dehydration of $H_4SiW_{12}O_{40}\cdot 15.6H_2O$ was studied *in situ* in the IR chamber. On evacuation at room temperature the departure of most loosely bonded water characterized by bands at 3550 and 1616 cm^{-1} was observed. In the remaining hexahydrate the band at 3445 cm^{-1} was ascribed to the hydrogen bond between the O_d oxygen atom of the Keggin unit and dioxonium $H_5O_2^+$ ion, the presence of which is manifested by the 1710 and 1100 cm^{-1} vibrations. All these bands vanish in the case of anhydrous $H_4SiW_{12}O_{40}$, in which the band at 3106 cm^{-1} ascribed to the hydrogen bond between neighbouring HPA anions $O_d–H^+–O_c$ is still present. The dehydration of hexahydrate is accompanied by splitting of the $W{=}O_d$ band into 987 and 1010 cm^{-1} reflecting the change of the kind of hydrogen bond in which the O_d oxygen atom is involved. Based on the above results it was concluded that protons forming oxonium ions in hydrated solid heteropoly acid are more strongly bonded than those in anhydrous one which are forming hydrogen bonds between neighbouring Keggin units.

Keywords: heteropoly acids, hydrates, tungstosilicic acid, hydrogen bond

1. Introduction

The hydrated solid dodecaheteropoly acids $H_{(8-x)}X^{x+}M_{12}O_{40}\cdot nH_2O$ may be represented as supramolecular systems in which solid heteropoly acid (HPA) plays the role of the host and water molecules occupying positions between HPA anions behave as the guest. The interactions between the guest and the host result in the hydration of protons and the formation of an array of hydrogen bonds between the hydrated protons, water molecules and HPA anions. Depending on the n value hydrates of different structure were obtained. For example, the structure of $H_3PW_{12}O_{40}\cdot 29H_2O$ is cubic diamond like, $H_3PW_{12}O_{40}\cdot 21H_2O$ is orthorhombic and $H_3PW_{12}O_{40}\cdot 6H_2O$ cubic bcc [1]. X-ray and neutron diffraction studies enabled to determine the positions of water molecules in the crystal lattice and basing on the interatomic distances to propose conclusions concerning the localization of hydrogen bonds. In particular, this has been done for $H_3PW_{12}O_{40}\cdot 21H_2O$ [2] and $H_3PW_{12}O_{40}\cdot 6H_2O$ [3]. In the latter case it has been stated [3] that dioxonium ion $H_5O_2^+$ links four neighbouring Keggin anions by forming hydrogen bonds with terminal $W{=}O_d$ oxygens (figure 1).

The hexahydrates isomorphous with $H_3PW_{12}O_{40}\cdot 6H_2O$ exist also in other dodecaheteropoly acids such as tungstosilicic and tungstoboric acids. Only three of four protons in the first case and three of five in the second one form dioxonium ions and hence their proper formulas are $(H_5O_2^+)_3(HSiW_{12}O_{40}^{3-})$ and $(H_5O_2^+)_3(H_2BW_{12}O_{40}^{3-})$. Brown et al. [3] suggest that such non-hydrated extra protons would occupy the positions between the terminal O_d oxygen of a Keggin unit and the bridging O_c oxygen of the neighbouring HPA anion thus forming a hydrogen bond.

It may be supposed that on dehydration protons bonded in dioxonium ions migrate to the positions of the “extra” protons, giving as a result changes in the IR spectrum in the 3200–3600 cm^{-1} range typical for the hydrogen bond. In fact, the authors of paper [4], who investigated the dehydration of $H_3PMo_{12}O_{40}$ with FTIR spectroscopy, reported that the loss of water molecules was accompanied by vanishing of the 3560 cm^{-1} band and appearance of a band at 3200 cm^{-1} in the region of hydrogen bond vibrations. Simultaneously, splitting of the stretching vibration band of the $Mo{=}O_d$ group at 960 cm^{-1} was observed. The aim of the present investigation was to study these effects in a more detailed way in hydrated $H_4SiW_{12}O_{40}$.

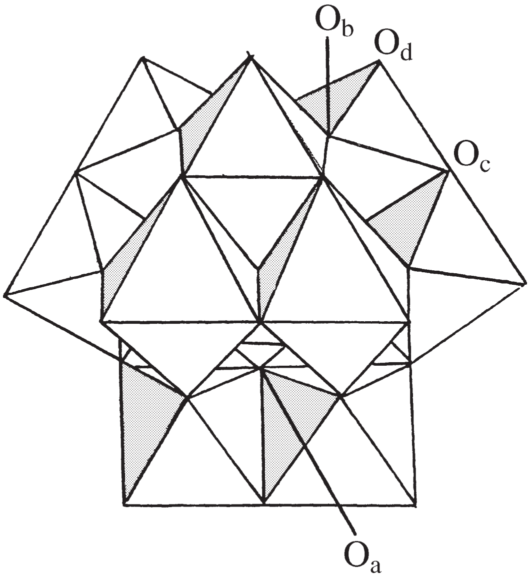

Figure 1. The structure of anion of dodecaheteropoly acids (Keggin unit).

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The study of the behaviour of protons in solid heteropoly acids and their interactions with absorbed water molecules is also interesting from the catalytic point of view. In particular bonding of protons by water molecules may influence the course of catalytic hydration of olefins. The present paper describes a FTIR study of sorption of water on solid $H_4SiW_{12}O_{40}$, which was also used as the catalyst in our previous research on isobutene hydration to *tert*-butyl alcohol [5].

2. Experimental

FTIR spectra were recorded with a Bruker IFS 48 spectrometer equipped with an MCT detector. The heteropoly acid sample for spectral investigation was prepared by evaporating a few drops of an aqueous solution of $H_4SiW_{12}O_{40}$ ($H_4SiW_{12}O_{40}\cdot 23.7H_2O$ Fluka p.p.a.) on a polished silicon wafer. The sample exposed to the atmosphere lost partially its water of crystallization and reached the $H_4SiW_{12}O_{40}\cdot 15.6H_2O$ composition. The thickness of the obtained layer was estimated to be about 0.2 mm (3 mg/cm^2). Both, evacuating and heating the sample, were carried out *in situ* in an IR cell as well as in a quartz spring sorption microbalance with a 50 mg sample of HPA.

3. Results

The spectrum of the sample equilibrated with atmospheric humidity at room temperature and the one recorded after 30 s evacuation at room temperature are presented as curves (a) and (b) in figures 2 and 3. An analogous experiment was carried out with the use of a vacuum microbalance and showed that the sample of $H_4SiW_{12}O_{40}\cdot 15.6H_2O$ (equilibrated with atmospheric humidity) lost 7.3 molecules of H_2O during 30 s evacuation and its composition became $H_4SiW_{12}O_{40}\cdot 8.3H_2O$. Next, the sample in the IR cell was slowly heated under vacuum (0.8 deg/min) up to 373 K. The IR spectra recorded after such a heating are presented as curves (c) in figures 2 and 3. The results of the vacuum microbalance experiment, in which the sample was heated according to the same program, showed that the sample composition at 373 K corresponded to anhydrous $H_4SiW_{12}O_{40}$. No further loss of mass was observed after heating up to 523 K.

In order to obtain more information on the spectral changes accompanying the dehydration, subtraction of spectra was performed and the results are presented in figure 2: the spectrum after evacuation at room temperature minus the spectrum of hydrated sample (curve (d)) as well as the spectrum after heating at 373 K minus the spectrum of the sample evacuated at room temperature (curve (e)).

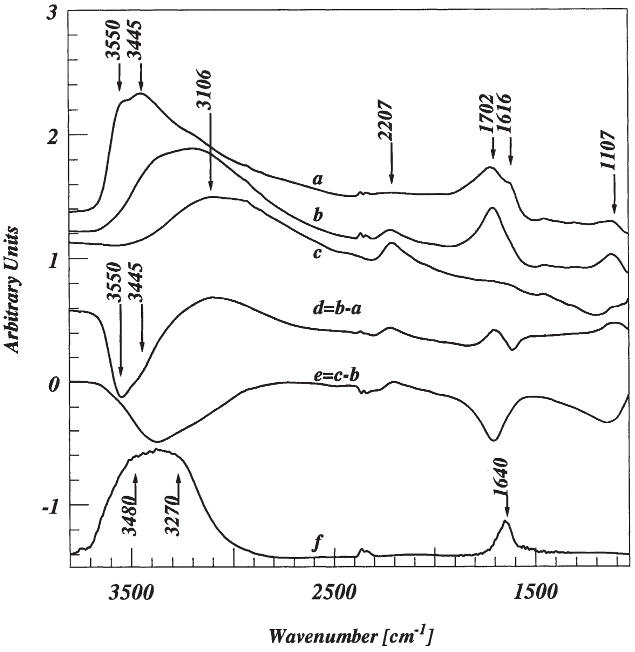

Figure 2. The IR spectra of dodecatungstosilicic acid in the range 3800–950 cm^{-1}: (a) spectrum of hydrated sample; (b) spectrum after 30 s evacuation; (c) spectrum of dehydrated sample (evacuation at 373 K); (d) difference spectrum (spectrum (b) minus spectrum (a)); (e) difference spectrum (spectrum (c) minus spectrum (b)); (f) spectrum of liquid water.

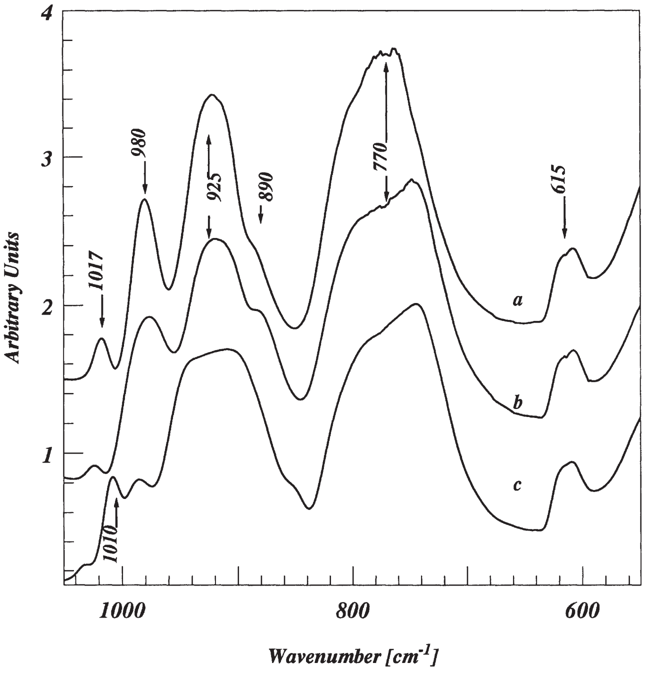

Figure 3. The IR spectra of dodecatungstosilicic acid in the range 1030–555 cm^{-1}: (a) spectrum of hydrated sample; (b) spectrum after 30 s evacuation; (c) spectrum of dehydrated sample (evacuation at 373 K).

TG and DTA analyses of $H_4SiW_{12}O_{40}\cdot 23.7H_2O$ were also done and the results are presented in figure 4. Four endothermic effects (at 346, 357, 394 and 510 K) as well as one exothermic effect at 793 K are present in the DTA curve. The low-temperature effect (at 346 K – the shoulder on the DTA curve) corresponds to incongruent sample fusion and is not accompanied by any distinct effect in the TG curve. A continuous loss of weight was observed upon heating up to 357 K; a small plateau correspond-

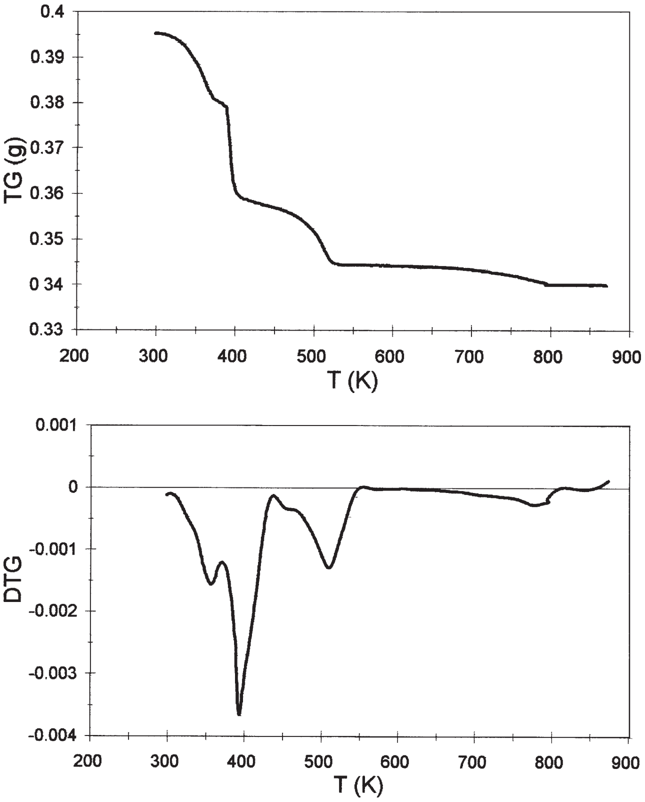

Figure 4. The TG and DTA curves of dehydration of $H_4SiW_{12}O_{40}\cdot 23.7H_2O$.

ing to $H_4SiW_{12}O_{40}\cdot 17.3H_2O$ appears at this temperature. A subsequent rapid weight loss was accompanied by an endothermic effect at 394 K, and resulted in the formation of the hexahydrate $H_4SiW_{12}O_{40}\cdot 6H_2O$, which was stable up to about 473 K when the last step of dehydration (endothermic effect at 510 K) leading to anhydrous $H_4SiW_{12}O_{40}$ occurred. It should be noted that, according to the results obtained in the vacuum desorption experiments, lower hydrates may be also formed at room temperature and that hexahydrate was the most stable under these conditions.

4. Discussion

The spectrum of the sample equilibrated with atmospheric humidity (figure 2, curve (a)) shows a strong and broad band with two submaxima: 3445 and 3550 cm^{-1}, a band at 1702 cm^{-1} with a shoulder at 1616 cm^{-1}, a band at 1107 cm^{-1} and a weak band at 2207 cm^{-1}. The latter band (at 2207 cm^{-1}), which was never observed in spectra recorded with a KBr pellet, is probably due to interactions between HPA and the silicon disc. The evacuation at room temperature resulted (figure 2, curve (b)) in a decrease of the band around 3445 cm^{-1} and its shift to a lower frequency. The analysis of the difference spectrum (figure 2, curve (d)) shows that the changes of the band around 3445 cm^{-1} are realised by the disappearance of the 3550 cm^{-1} maximum, in a decrease of the maximum at 3445 cm^{-1} (the shoulder in the negative peak), and in an increase of the maximum at 3106 cm^{-1}. The evacuation at room temperature results also in the disappearance of the 1616 cm^{-1} band. These effects are due to a loss of loosely bonded water.

It is interesting to mention, that the values of both O–H vibrations (stretching $\nu_{O\text{–}H}$ and δ_{H_2O} bending of loosely bonded water) 3550 and 1616 cm^{-1} are intermediate between the analogous values for water in gas (ν_{as} 3755, ν_{sym} 3656 and 1595 cm^{-1}) and liquid phase (3220–3480 and 1640 cm^{-1}). The O–H$\cdots$O band of loosely bonded water about 3550 cm^{-1} (figure 2, curve (d)) is more narrow than that of liquid water (figure 2, curve (f)). It suggests, that water loosely bonded with HPA is in an intermediate state between gas (free molecules) and liquid (hydrogen bonding). It is possible, that in the case of loosely bonded water, the hydrogen bonds are longer and weaker than in liquid water. According to the results of the microbalance experiment, the amount of such loosely bonded water in the initial sample was 7.3 H_2O per Keggin unit.

According to the results presented in figure 2, spectra of hydrated HPA show, apart from the bands of loosely bonded water, also the bands at 1107, 1702 and 3445 cm^{-1}, which are stable upon the evacuation at room temperature, but disappear upon evacuation at 373 K. They are characteristic of water molecules which are more strongly bonded with HPA. According to [6], the bands at 1710 and about 1100 cm^{-1} are due to oxonium ions (H_3O^+) or more likely to dioxonium ions ($H_5O_2^+$), the existence of which has been reported in hexahydrates of dodecaheteropoly acids [3]. In our case, the results of microbalance experiments showed that hexahydrate was the predominant phase upon dehydration of dodecatungstosilic acid at room temperature. According to [3], the dioxonium ions in hexahydrates are hydrogen-bonded to W=O_d oxygens of four neighbouring HPA anions. It suggests that the IR band at 3445 cm^{-1} is due to such a hydrogen bonding.

Figure 2 (curve (c)) represents the spectrum of the completely dehydrated HPA (after evacuation at 373 K). The absence of any form of adsorbed water is evidenced by the absence of the 1616 and 1702 cm^{-1} bands. Therefore, the broad band at 3106 cm^{-1} may be assigned to $O_d\cdots H\cdots O_c$ hydrogen bonds between the neighbouring Keggin units, as it was postulated in [3] on the basis of X-ray and neutron diffraction studies.

Further information on the bond between Keggin units can be obtained from the spectrum of HPA anion in the 555–1100 cm^{-1} region. Six IR bands are present in the spectrum of the fully hydrated sample: 615, 770, 890, 925, 980, and 1017 cm^{-1} (figure 3). The assignment of some of them is based on literature data [1,7]. The bands at 770 and 890 cm^{-1} were assigned to stretching of tungsten–oxygen–tungsten chains, the former to W–O_c–W, and the latter to W–O_b–W. The O_c oxygen atom is common for two [WO_6] octahedra in [W_3O_{10}] subunits, joined by O_b atoms. The band at 925 cm^{-1} was assigned to Si–O_a stretching (there are four O_a atoms connected to the central Si atom). The band at 980 cm^{-1} corresponds to the W=O_d bond, where

O_d is the terminal oxygen atom (figure 1). The assignments of the 615 and 1017 cm^{-1} bands are not known.

The first step of dehydration (evacuation at room temperature) removed, as described above, loosely bonded water. No distinct changes in the spectrum of the Keggin unit were observed (except for a small bathochromic shift of the $W–O_c–W$ band). It should be noted that in the $H_4SiW_{12}O_{40}$ hexahydrate oxygen atom in the $W{=}O_d$ group, of which the band at 980 cm^{-1} is characteristic, participates in hydrogen bonding with dioxonium ions (OH vibration at 3445 cm^{-1} figure 2, curve (b)). The evacuation at 373 K removed dioxonium ions and, therefore, the 3445 cm^{-1} band disappeared (figure 2, curves (c) and (e)). Simultaneously the band at 980 cm^{-1} split into two bands, at 987 cm^{-1} assigned to $W{=}O_d$ groups, the oxygen of which participates in the hydrogen bond $O_d \cdots H \cdots O_c$ between two neighbouring Keggin units, and 1010 cm^{-1} assigned to $W{=}O_d$ bonds not participating in hydrogen bond formation (figure 3, curve (c)). The formation of the hydrogen bond between Keggin units accompanied the appearance of the band at 3106 cm^{-1} (figure 2, curve (c)). As mentioned in the introduction, it has been found [3] that such hydrogen bonds are not to be expected in hexahydrate of tungstophosphoric acid $(H_5O_2^+)_3(PW_{12}O_{40}^{3-})$, but they should be present in hexahydrate of tungstenosilicic acid $(H_5O_2^+)_3(HSiW_{12}O_{40}^{3-})$.

Two kinds of hydrogen bonds $O_d–H \cdots O_{ox}$ (O_{ox} oxygen atom in dioxonium ion) and $O_d \cdots H \cdots O_c$, characterized by O–H stretching frequencies at 3445 and 3106 cm^{-1}, differ in their strength. In the case of $O_d–H \cdots O_{ox}$, the hydrogen bond is weaker (higher O–H frequency) and the proton is more strongly held than in $O_d–H \cdots O_c$. Protons are, therefore, more strongly held in the hydrated heteropoly acid than in its anhydrous form. The possible consequences of this for the catalytic properties of solid heteropoly acids will be discussed in a further paper.

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